

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-350154

(43)Date of publication of application : 22.12.1994

(51)Int.Cl.

H01L 41/08
C01G 25/00
H01L 37/02
// G01J 1/02

(21)Application number : 05-137892

(71)Applicant : SEIKO EPSON CORP

(22)Date of filing : 08.06.1993

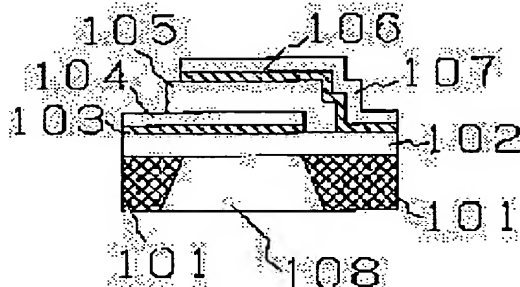
(72)Inventor : SHIMADA KATSUTO

(54) PIEZOELECTRIC THIN FILM ELEMENT

(57)Abstract:

PURPOSE: To improve piezoelectric characteristic, ferroelectric characteristic and pyroelectric characteristic by using a PZT thin film having optimum crystal line orientation property and composition.

CONSTITUTION: A titanate zirconate (PZT) film 105 whose chemical formula is $Pb_{1+y}(Zr_xTi_{1-x})O_{3+y}$, composition rate is in the range of $0 \leq x \leq 0.55$ and $0 \leq y \leq 0.5$ and crystal structure is rhombohedron system is formed on a substrate 101 wherein a $\langle 111 \rangle$ orientation metallic film 104 is formed. A $\langle 111 \rangle$ orientation degree of the PZT film 105 to a main surface vertical direction of the substrate 101 is 70% or more. Otherwise, a PZT film 105 whose chemical formula is $Pb_{1+y}(Zr_xTi_{1-x})O_{3+y}$, composition rate is in the range of $0.55 \leq x \leq 1$ and $0 \leq y \leq 0.5$ and crystal structure is tetragonal system is orientated on the substrate 101 wherein the $\langle 100 \rangle$ orientation metallic film 104 is formed. A $\langle 001 \rangle$ orientation degree of the PZT film 105 to a main surface vertical direction of the substrate 101 is 70% or more.



LEGAL STATUS

[Date of request for examination]

06.06.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3341357

[Date of registration]

23.08.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's

decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

JP0 and NCIP1 are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The piezo electric crystal thin film which a presentation ratio has a chemical formula by $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$ on the substrate with which the metal membrane was formed in the range of $0 \leq X < 0.55$ and $0 \leq Y \leq 0.5$, and a crystal structure is the titanite-acid lead zirconate film of a rhombohedral system, and is characterized by the $\langle 111 \rangle$ amounts of preferred orientation of said titanite-acid lead zirconate film being 70% or more to the principal plane perpendicular direction of said substrate.

[Claim 2] The piezo electric crystal thin film according to claim 1 which a metal membrane is platinum (Pt), gold (Au), or film that uses Pt or Au as a principal component, and is characterized by being $\langle 111 \rangle$ orientation film to the principal plane perpendicular direction of said substrate.

[Claim 3] The piezo electric crystal thin film which a presentation ratio has a chemical formula by $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$ on the substrate with which the metal membrane was formed in the range of $0.55 \leq X < 1$ and $0 \leq Y \leq 0.5$, and a crystal structure is the titanite-acid lead zirconate film of tetragonal system, and is characterized by the $\langle 001 \rangle$ amounts of preferred orientation of said titanite-acid lead zirconate film being 70% or more to the principal plane perpendicular direction of said substrate.

[Claim 4] The piezo electric crystal thin film according to claim 3 which a metal membrane is platinum (Pt), gold (Au), or film that uses Pt or Au as a principal component, and is characterized by being $\langle 100 \rangle$ orientation film to the principal plane perpendicular direction of said substrate.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the ferroelectric thin-film device used for piezoelectric devices, such as a thin film piezoelectric transducer and a fluid injector, a semiconductor memory, a pyroelectric infrared detector, etc.

[0002]

[Description of the Prior Art] As for the conventional technique in connection with this invention, JP, 62-252005, A is indicated.

[0003] According to said conventional technique, when a chemical formula is $Pb_{1+Y}(Zr_XTi_{1-X})O_{3+Y}$, the presentation ratio is limited to the range of $0 \leq X < 0.55$ and $Y = 0$, and in the titanate-acid lead zirconate (PZT) of the polycrystalline substance of bulk, the crystal structure was limited to stoichiometric composition of tetragonal system.

[0004] Furthermore, Zr presentation ratio X is restricted to the range of 0 to 0.55, and 75% or more of the spontaneous polarization of the domain in the crystal grain of PZT had turned to the one direction.

[0005]

[Problem(s) to be Solved by the Invention] However, the trouble shown below exists in the ferroelectric thin film using said conventional technique.

[0006] Since Pb presentation ratios of PZT are $Pb/(Zr+Ti) = 1$ and stoichiometric composition, the manufacture approach is difficult.

[0007] Especially the thing that in the case of the compound containing Pb it is the form of PbO , is easy to escape from Pb at the time of high temperature processing at the time of membrane formation of baking, sintering, or a spatter, and is controlled to stoichiometric composition at it is dramatically difficult.

[0008] Furthermore, in almost all piezoelectric devices, a semiconductor memory, and a pyroelectric infrared-detector component, since carrying out polarization processing after membrane formation is allowed, Zr presentation ratio X does not need to be restricted to the range of $0 \leq X < 0.55$.

[0009] Then, the place which this invention solves such a technical problem and is made into the object is improving a piezo-electric property, a ferroelectric property, and a pyroelectric property using a PZT thin film with the optimal crystal stacking tendency and the optimal presentation.

[0010]

[Means for Solving the Problem] In order to solve the above-mentioned trouble, the piezo electric crystal thin film of (1) this invention A chemical formula on the substrate with which the metal membrane was formed by $Pb_{1+Y}(Zr_XTi_{1-X})O_{3+Y}$ A presentation ratio is in the range of $0 \leq X < 0.55$ and $0 \leq Y \leq 0.5$, and a crystal structure is the titanate-acid lead zirconate film of a rhombohedral system, and it is characterized by the $\langle 111 \rangle$ amounts of preferred orientation of said titanate-acid lead zirconate film being 70% or more to the principal plane perpendicular direction of said substrate.

[0011] (2) It is still more desirable for the above-mentioned metal membrane to be platinum (Pt), gold (Au), or film that uses Pt or Au as a principal component, and to be $\langle 111 \rangle$ orientation film to

the principal plane perpendicular direction of said substrate.

[0012] Or on the substrate with which the metal membrane was formed, a chemical formula is $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$, and the piezo electric crystal thin film of (3) this inventions has a presentation ratio in the range of $0.55 \leq X < 1$ and $0 \leq Y \leq 0.5$, and a crystal structure is the titanate-acid lead zirconate film of tetragonal system, and it is characterized by the $\langle 001 \rangle$ amounts of preferred orientation of said titanate-acid lead zirconate film being 70% or more to the principal plane perpendicular direction of said substrate.

[0013] (4) It is still more desirable for the above-mentioned metal membrane to be platinum (Pt), gold (Au), or film that uses Pt or Au as a principal component, and to be $\langle 100 \rangle$ orientation film to the principal plane perpendicular direction of said substrate.

[0014]

[Example] (Example 1) The example of this invention is hereafter explained based on a drawing.

[0015] Drawing 1 is the sectional view of the thin film piezoelectric transducer which is the 1st example of the ferroelectric thin film created according to this invention.

[0016] (100) Oxidize thermally to the field single crystal Si substrate 101, and form SiO_2 1-micrometer film 102 in it.

[0017] On said SiO_2 film 102, the Pt lower electrode 104 of the Ti layer 103 of thickness 50Å and thickness 3000Å was formed by DC sputtering.

[0018] The sputter was performed at Ar ambient atmosphere and the substrate temperature of 200 degrees C.

[0019] The Pt lower electrode 104 is carried out $\langle 111 \rangle$ orientation to the principal plane perpendicular direction of the Si substrate 101.

[0020] Next, the PZT film 105 was formed by 2 micrometers and the RF sputter.

[0021] The sputter was performed at Ar, O_2 ambient atmosphere, and the substrate temperature of 200 degrees C.

[0022] $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$ was used for the sputtering target.

[0023] Here, it is $Y = 0.3$ and $X = 0.5$.

[0024] Subsequently, in order to obtain PZT of the perovskite crystal structure, heat treatment was performed at 600 degrees C among O_2 ambient atmosphere for 3 hours.

[0025] Subsequently, the sequential vacuum evaporation of the Ti layer 106 of thickness 100Å and the Au electrode 107 of thickness 2000Å was carried out on the PZT film, opening 108 was formed in the last until it resulted in the single crystal Si substrate 101 in the lower part of the PZT film 105 at SiO_2 film 102, and the ferroelectric thin film was created.

[0026] The X diffraction pattern of a typical PZT thin film is shown in drawing 2.

[0027] Except the reflective peak of Si substrate, and the reflective peak of Pt lower electrode, it is the reflective peak of PZT of a perovskite structure.

[0028] 0.05 and Zr presentation ratio X of the superfluous lead presentation ratio Y of this example shown in drawing 2 were 0.50, and the $\langle 111 \rangle$ amounts of preferred orientation were 80%.

[0029] Here, the $\langle 111 \rangle$ amount of preferred orientation P (111) is expressed with $P(111) = I(111)/\sigma_{\text{total}}(hkl)$.

[0030] $\sigma_{\text{total}}(hkl)$ — an X diffraction (XRD) — it is the angle-of-elevation reflection method of law, and 2θ when using CuK alpha rays for wavelength expresses the sum of the total diffraction reinforcement of PZT which is 20 – 80 degrees.

[0031] Specifically, it is total of (100), (110), (111), (210), (211), (221), and crystal-face (310) reflectivity.

[0032] Similarly $I(111)$ expresses the crystal-face (111) reflectivity of PZT.

[0033] Drawing 3 shows the Zr presentation ratio X dependency of the piezoelectric constant d_{31} of the PZT thin film of 2 micrometers of thickness which carried out orientation in the $\langle 111 \rangle$ directions 100% from 70.

[0034] The overPbO presentation ratio Y is 0.05.

[0035] The piezoelectric constant of bulk PZT was also shown for the comparison in drawing 3.

[0036] As shown in drawing 3, in all presentation range, the piezoelectric constant of the PZT thin film carried out 70 to 100% $\langle 111 \rangle$ orientation [piezoelectric constant / of PZT of bulk] showed the big value.

[0037] Especially, Zr presentation ratio X showed the large value by leaps and bounds in the range of 0 to 0.55 as compared with bulk PZT.

[0038] It is thought that it is because it becomes a rhombohedral system in the case of an orientation thin film to the crystal structure of bulk PZT being this presentation range, and there being this with tetragonal system.

[0039] That is, although a piezoelectric constant becomes large so that the presentation ratio X is [the range X of the rhombohedral system presentation of bulk PZT, i.e., Zr presentation ratio,] small in 0.55 to 1, it will be because X has reached to the range of 0 to 0.55 further in the case of the thin film.

[0040] The overPbO presentation ratio Y dependency of the piezoelectric constant d31 at the time of fixing to Zr presentation ratio X= 0.45 is shown in drawing 4 .

[0041] The thickness of a PZT thin film is the same and 2 micrometers and the <111> amounts of preferred orientation are 70 to 100%.

[0042] As shown in drawing 4 , the piezoelectric constant d31 is greatly dependent on the superfluous part Y of PbO, if Y is smaller than 0, will fall rapidly and will fall from Y= 0.5 to the bulk PZT average in size.

[0043] As a reason a piezoelectric constant 31 will become small if Y becomes larger than 0.5, it turned out that it is the deposit of PbO to a grain boundary.

[0044] Therefore, as for the range of Y, it is desirable that it is [or more 0] 0.5 or less.

[0045] Although explained in the example 1, using the <111> orientation Pt as a lower electrode, other metal membranes are [that the <111> amounts of preferred orientation of a PZT thin film should just become 70% or more] above sufficient as Au, Pt-Ir, Pt-Pd, Pt-nickel, Pt-Ti, etc.

[0046] Furthermore, although the example 1 explained taking the case of the thin film piezoelectric transducer, it is obvious that it is applicable to a fluid injector, a semiconductor memory, a pyroelectric infrared detector, etc. as it is.

[0047] (Example 2) The example of this invention is hereafter explained based on a drawing.

[0048] Drawing 5 is the sectional view of the 2nd example of the ferroelectric thin film created according to this invention.

[0049] (100) Form the Pt lower electrode 202 of <100> orientation in the field single crystal MgO substrate 201 to the direction of a principal plane of the MgO substrate 201 by the RF spatter.

[0050] The spatter was performed at the substrate temperature of 200 degrees C among the ambient atmosphere of Ar/O2=8/2.

[0051] Next, the PZT film 203 was formed by 2 micrometers and the RF spatter.

[0052] The spatter was performed at Ar, O2 ambient atmosphere, and the substrate temperature of 700 degrees C.

[0053] $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$ was used for the sputtering target.

[0054] Here, it is Y= 0.5 and X= 0.6.

[0055] By the elevated-temperature spatter, PZT of the perovskite crystal structure was able to be obtained by the AZU-spatter.

[0056] Subsequently, the sequential vacuum evaporation of the Ti layer 204 of thickness 100A and the Au electrode 205 of thickness 2000A was carried out on the PZT film, and the property was evaluated.

[0057] The X diffraction pattern of a typical PZT thin film is shown in drawing 6 .

[0058] Except the reflective peak of a MgO single crystal substrate, and the reflective peak of Pt electrode, it is the reflective peak of PZT of a perovskite structure.

[0059] 0.10 and Zr presentation ratio X of the superfluous lead presentation ratio Y of this example shown in drawing 6 were 0.60, and the <001> amounts of preferred orientation were 98%.

[0060] Here, the <001> amount of preferred orientation P (001) is expressed with $P(001) = I(001)/\sum I(hkl)$.

[0061] Drawing 7 shows the Zr presentation ratio X dependency of the specific inductive capacity epsilon of the PZT thin film of 2 micrometers of thickness which carried out orientation in the <001> directions 100% from 70.

[0062] The specific inductive capacity epsilon shown here is the specific inductive capacity of the direction of thickness after carrying out polarization processing in the direction of thickness.

[0063] The overPbO presentation ratio Y is 0.10.

[0064] The specific inductive capacity epsilon of bulk PZT was shown for the comparison in drawing 7.

[0065] As shown in drawing 7, in all presentation range, the specific inductive capacity epsilon of the PZT thin film carried out 70 to 100% <001> orientation [specific inductive capacity / epsilon / of PZT of bulk] showed the big value.

[0066] Especially, Zr presentation ratio X showed the large value by leaps and bounds in the range of 0.55 to 1 as compared with bulk PZT.

[0067] It is thought that it is because it becomes tetragonal system in the case of an orientation thin film to the crystal structure of bulk PZT being this presentation range, and there being this with a rhombohedral system.

[0068] That is, although specific inductive capacity becomes large so that the presentation ratio X is [the range X of the tetragonal-system presentation of bulk PZT, i.e., Zr presentation ratio,] large in 0 to 0.55, it will be because X has reached to the range of 0.55 to 1 further in the case of the thin film.

[0069] The overPbO presentation ratio Y dependency of the specific inductive capacity epsilon at the time of fixing to drawing 8 at Zr presentation ratio X= 0.60 is shown.

[0070] The thickness of a PZT thin film is the same and 2 micrometers and the <001> amounts of preferred orientation are 95 to 100%.

[0071] The specific inductive capacity of bulk PZT is also shown for a comparison.

[0072] As shown in drawing 8, it is greatly dependent on the superfluous part Y of PbO, and if specific inductive capacity epsilon has Y smaller than 0, it will fall rapidly and will fall from Y= 0.5 to the bulk PZT average or less than [it] in size.

[0073] Therefore, as for the range of Y, it is desirable that it is [or more 0] 0.5 or less.

[0074] Although explained in the example 2, using the <100> orientation Pt as a lower electrode, other metal membranes are [that the <001> amounts of preferred orientation of a PZT thin film should just become 70% or more] above sufficient as Au, Pt-Ir, Pt-Pd, Pt-nickel, Pt-Ti, etc.

[0075] Above, although explained as a piezoelectric film in the above-mentioned examples 1 and 2 using the PZT thin film of a pure presentation, even if some impurity is mixed, of course, it does not interfere.

[0076] As an impurity, it is possible for there to be Nb, La, Ta, Nd, W, Mo, Mn, Ba, Sr, calcium, Bi, etc., and to add less than [15 mol %] as what generally improves piezoelectric.

[0077]

[Effect of the Invention] As stated above, the piezo electric crystal thin film of this invention has the following effectiveness. Since a piezo-electric property, a ferroelectric property, and a pyroelectric property can be improved by leaps and bounds as compared with PZT of bulk by using a PZT thin film with the optimal crystal stacking tendency and the optimal presentation, and it is a thin film further and can manufacture by the spatter, a chemical-vapor-deposition method, etc., creation is easy and it can apply to piezoelectric devices, such as a thin film piezoelectric transducer and a fluid injector, a semiconductor memory, a pyroelectric infrared detector, etc.

[Translation done.]

*** NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Industrial Application] This invention relates to the ferroelectric thin-film device used for piezoelectric devices, such as a thin film piezoelectric transducer and a fluid injector, a semiconductor memory, a pyroelectric infrared detector, etc.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] As for the conventional technique in connection with this invention, JP,62-252005,A is indicated.

[0003] According to said conventional technique, when a chemical formula is $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$, the presentation ratio is limited to the range of $0 \leq X < 0.55$ and $Y = 0$, and in the titanate-acid lead zirconate (PZT) of the polycrystalline substance of bulk, the crystal structure was limited to stoichiometric composition of tetragonal system.

[0004] Furthermore, Zr presentation ratio X is restricted to the range of 0 to 0.55, and 75% or more of the spontaneous polarization of the domain in the crystal grain of PZT had turned to the one direction.

[Translation done.]

*** NOTICES ***

JPO and NCIP1 are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] As stated above, the piezo electric crystal thin film of this invention has the following effectiveness. Since a piezo-electric property, a ferroelectric property, and a pyroelectric property can be improved by leaps and bounds as compared with PZT of bulk by using a PZT thin film with the optimal crystal stacking tendency and the optimal presentation, and it is a thin film further and can manufacture by the spatter, a chemical-vapor-deposition method, etc., creation is easy and it can apply to piezoelectric devices, such as a thin film piezoelectric transducer and a fluid injector, a semiconductor memory, a pyroelectric infrared detector, etc.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, the trouble shown below exists in the ferroelectric thin film using said conventional technique.

[0006] Since Pb presentation ratios of PZT are $Pb/(Zr+Ti) = 1$ and stoichiometric composition, the manufacture approach is difficult.

[0007] Especially the thing that in the case of the compound containing Pb it is the form of PbO, is easy to escape from Pb at the time of high temperature processing at the time of membrane formation of baking, sintering, or a spatter, and is controlled to stoichiometric composition at it is dramatically difficult.

[0008] Furthermore, in almost all piezoelectric devices, a semiconductor memory, and a pyroelectric infrared-detector component, since carrying out polarization processing after membrane formation is allowed, Zr presentation ratio X does not need to be restricted to the range of $0 \leq X < 0.55$.

[0009] Then, the place which this invention solves such a technical problem and is made into the object is improving a piezo-electric property, a ferroelectric property, and a pyroelectric property using a PZT thin film with the optimal crystal stacking tendency and the optimal presentation.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] In order to solve the above-mentioned trouble, the piezo electric crystal thin film of (1) this invention A chemical formula on the substrate with which the metal membrane was formed by $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$ A presentation ratio is in the range of $0 \leq X < 0.55$ and $0 \leq Y \leq 0.5$, and a crystal structure is the titanate-acid lead zirconate film of a rhombohedral system, and it is characterized by the $\langle 111 \rangle$ amounts of preferred orientation of said titanate-acid lead zirconate film being 70% or more to the principal plane perpendicular direction of said substrate.

[0011] (2) It is still more desirable for the above-mentioned metal membrane to be platinum (Pt), gold (Au), or film that uses Pt or Au as a principal component, and to be $\langle 111 \rangle$ orientation film to the principal plane perpendicular direction of said substrate.

[0012] Or on the substrate with which the metal membrane was formed, a chemical formula is $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$, and the piezo electric crystal thin film of (3) this inventions has a presentation ratio in the range of $0.55 \leq X < 1$ and $0 \leq Y \leq 0.5$, and a crystal structure is the titanate-acid lead zirconate film of tetragonal system, and it is characterized by the $\langle 001 \rangle$ amounts of preferred orientation of said titanate-acid lead zirconate film being 70% or more to the principal plane perpendicular direction of said substrate.

[0013] (4) It is still more desirable for the above-mentioned metal membrane to be platinum (Pt), gold (Au), or film that uses Pt or Au as a principal component, and to be $\langle 100 \rangle$ orientation film to the principal plane perpendicular direction of said substrate.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

EXAMPLE

[Example] (Example 1) The example of this invention is hereafter explained based on a drawing.

[0015] Drawing 1 is the sectional view of the thin film piezoelectric transducer which is the 1st example of the ferroelectric thin film created according to this invention.

[0016] (100) Oxidize thermally to the field single crystal Si substrate 101, and form SiO₂ 1- micrometer film 102 in it.

[0017] On said SiO₂ film 102, the Pt lower electrode 104 of the Ti layer 103 of thickness 50A and thickness 3000A was formed by DC sputtering.

[0018] The spatter was performed at Ar ambient atmosphere and the substrate temperature of 200 degrees C.

[0019] The Pt lower electrode 104 is carried out <111> orientation to the principal plane perpendicular direction of the Si substrate 101.

[0020] Next, the PZT film 105 was formed by 2 micrometers and the RF spatter.

[0021] The spatter was performed at Ar, O₂ ambient atmosphere, and the substrate temperature of 200 degrees C.

[0022] Pb_{1+Y}(Zr_XTi_{1-X}) O_{3+Y} was used for the sputtering target.

[0023] Here, it is Y= 0.3 and X= 0.5.

[0024] Subsequently, in order to obtain PZT of the perovskite crystal structure, heat treatment was performed at 600 degrees C among O₂ ambient atmosphere for 3 hours.

[0025] Subsequently, the sequential vacuum evaporations of the Ti layer 106 of thickness 100A and the Au electrode 107 of thickness 2000A was carried out on the PZT film, opening 108 was formed in the last until it resulted in the single crystal Si substrate 101 in the lower part of the PZT film 105 at SiO₂ film 102, and the ferroelectric thin film was created.

[0026] The X diffraction pattern of a typical PZT thin film is shown in drawing 2.

[0027] Except the reflective peak of Si substrate, and the reflective peak of Pt lower electrode, it is the reflective peak of PZT of a perovskite structure.

[0028] 0.05 and Zr presentation ratio X of the superfluous lead presentation ratio Y of this example shown in drawing 2 were 0.50, and the <111> amounts of preferred orientation were 80%.

[0029] Here, the <111> amount of preferred orientation P (111) is expressed with $P(111) = I(111)/\sigma I(hkl)$.

[0030] $\sigma I(hkl)$ — an X diffraction (XRD) — it is the angle-of-elevation reflection method of law, and 2theta when using CuK alpha rays for wavelength expresses the sum of the total diffraction reinforcement of PZT which is 20 – 80 degrees.

[0031] Specifically, it is total of (100), (110), (111), (210), (211), (221), and crystal-face (310) reflectivity.

[0032] Similarly I (111) expresses the crystal-face (111) reflectivity of PZT.

[0033] Drawing 3 shows the Zr presentation ratio X-dependency of the piezoelectric constant d₃₁ of the PZT thin film of 2 micrometers of thickness which carried out orientation in the <111> directions 100% from 70.

[0034] The overPbO presentation ratio Y is 0.05.

[0035] The piezoelectric constant of bulk PZT was also shown for the comparison in drawing 3.

[0036] As shown in drawing 3, in all presentation range, the piezoelectric constant of the PZT thin

film carried out 70 to 100% $\langle 111 \rangle$ orientation [piezoelectric constant / of PZT of bulk] showed the big value.

[0037] Especially, Zr presentation ratio X showed the large value by leaps and bounds in the range of 0 to 0.55 as compared with bulk PZT.

[0038] It is thought that it is because it becomes a rhombohedral system in the case of an orientation thin film to the crystal structure of bulk PZT being this presentation range, and there being this with tetragonal system.

[0039] That is, although a piezoelectric constant becomes large so that the presentation ratio X is [the range X of the rhombohedral system presentation of bulk PZT, i.e., Zr presentation ratio,] small in 0.55 to 1, it will be because X has reached to the range of 0 to 0.55 further in the case of the thin film.

[0040] The overPbO presentation ratio Y dependency of the piezoelectric constant d31 at the time of fixing to Zr presentation ratio X= 0.45 is shown in drawing 4 .

[0041] The thickness of a PZT thin film is the same and 2 micrometers and the $\langle 111 \rangle$ amounts of preferred orientation are 70 to 100%.

[0042] As shown in drawing 4 , the piezoelectric constant d31 is greatly dependent on the superfluous part Y of PbO, if Y is smaller than 0, will fall rapidly and will fall from Y= 0.5 to the bulk PZT average in size.

[0043] As a reason a piezoelectric constant 31 will become small if Y becomes larger than 0.5, it turned out that it is the deposit of PbO to a grain boundary.

[0044] Therefore, as for the range of Y, it is desirable that it is [or more 0] 0.5 or less.

[0045] Although explained in the example 1, using the $\langle 111 \rangle$ orientation Pt as a lower electrode, other metal membranes are [that the $\langle 111 \rangle$ amounts of preferred orientation of a PZT thin film should just become 70% or more] above sufficient as Au, Pt-Ir, Pt-Pd, Pt-nickel, Pt-Ti, etc.

[0046] Furthermore, although the example 1 explained taking the case of the thin film piezoelectric transducer, it is obvious that it is applicable to a fluid injector, a semiconductor memory, a pyroelectric infrared detector, etc. as it is.

[0047] (Example 2) The example of this invention is hereafter explained based on a drawing.

[0048] Drawing 5 is the sectional view of the 2nd example of the ferroelectric thin film created according to this invention.

[0049] (100) Form the Pt lower electrode 202 of $\langle 100 \rangle$ orientation in the field single crystal MgO substrate 201 to the direction of a principal plane of the MgO substrate 201 by the RF spatter.

[0050] The spatter was performed at the substrate temperature of 200 degrees C among the ambient atmosphere of Ar/O₂=8/2.

[0051] Next, the PZT film 203 was formed by 2 micrometers and the RF spatter.

[0052] The spatter was performed at Ar, O₂ ambient atmosphere, and the substrate temperature of 700 degrees C.

[0053] Pb₁+Y(ZrXTi_{1-X}) O₃+Y was used for the sputtering target.

[0054] Here, it is Y= 0.5 and X= 0.6.

[0055] By the elevated-temperature spatter, PZT of the perovskite crystal structure was able to be obtained by the AZU-spatter.

[0056] Subsequently, the sequential vacuum evaporation of the Ti layer 204 of thickness 100Å and the Au electrode 205 of thickness 2000Å was carried out on the PZT film, and the property was evaluated.

[0057] The X diffraction pattern of a typical PZT thin film is shown in drawing 6 .

[0058] Except the reflective peak of a MgO single crystal substrate, and the reflective peak of Pt electrode, it is the reflective peak of PZT of a perovskite structure.

[0059] 0.10 and Zr presentation ratio X of the superfluous lead presentation ratio Y of this example shown in drawing 6 were 0.60, and the $\langle 001 \rangle$ amounts of preferred orientation were 98%.

[0060] Here, the $\langle 001 \rangle$ amount of preferred orientation P (001) is expressed with $P(001) = I(001)/\sigma I(hkl)$.

[0061] Drawing 7 shows the Zr presentation ratio X dependency of the specific inductive capacity epsilon of the PZT thin film of 2 micrometers of thickness which carried out orientation in the $\langle 001 \rangle$ directions 100% from 70.

[0062] The specific inductive capacity epsilon shown here is the specific inductive capacity of the direction of thickness after carrying out polarization processing in the direction of thickness.

[0063] The overPbO presentation ratio Y is 0.10.

[0064] The specific inductive capacity epsilon of bulk PZT was shown for the comparison in drawing 7.

[0065] As shown in drawing 7, in all presentation range, the specific inductive capacity epsilon of the PZT thin film carried out 70 to 100% <001> orientation [specific inductive capacity / epsilon / of PZT of bulk] showed the big value.

[0066] Especially, Zr presentation ratio X showed the large value by leaps and bounds in the range of 0.55 to 1 as compared with bulk PZT.

[0067] It is thought that it is because it becomes tetragonal system in the case of an orientation thin film to the crystal structure of bulk PZT being this presentation range, and there being this with a rhombohedral system.

[0068] That is, although specific inductive capacity becomes large so that the presentation ratio X is [the range X of the tetragonal-system presentation of bulk PZT, i.e., Zr presentation ratio,] large in 0 to 0.55, it will be because X has reached to the range of 0.55 to 1 further in the case of the thin film.

[0069] The overPbO presentation ratio Y dependency of the specific inductive capacity epsilon at the time of fixing to drawing 8 at Zr presentation ratio X= 0.60 is shown.

[0070] The thickness of a PZT thin film is the same and 2 micrometers and the <001> amounts of preferred orientation are 95 to 100%.

[0071] The specific inductive capacity of bulk PZT is also shown for a comparison.

[0072] As shown in drawing 8, it is greatly dependent on the superfluous part Y of PbO, and if specific inductive capacity epsilon has Y smaller than 0, it will fall rapidly and will fall from Y= 0.5 to the bulk PZT average or less than [it] in size.

[0073] Therefore, as for the range of Y, it is desirable that it is [or more 0] 0.5 or less.

[0074] Although explained in the example 2, using the <100> orientation Pt as a lower electrode, other metal membranes are [that the <001> amounts of preferred orientation of a PZT thin film should just become 70% or more] above sufficient as Au, Pt-Ir, Pt-Pd, Pt-nickel, Pt-Ti, etc.

[0075] Above, although explained as a piezoelectric film in the above-mentioned examples 1 and 2 using the PZT thin film of a pure presentation, even if some impurity is mixed, of course, it does not interfere.

[0076] As an impurity, it is possible for there to be Nb, La, Ta, Nd, W, Mo, Mn, Ba, Sr, calcium, Bi, etc., and to add less than [15 mol %] as what generally improves piezoelectric.

[Translation done.]

*** NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The sectional view of the thin film piezoelectric transducer in the example of this invention.

[Drawing 2] Drawing of the X diffraction pattern of the PZT thin film in the example of this invention.

[Drawing 3] Drawing showing the Zr presentation ratio X dependency of the piezoelectric constant d_{31} of the example of this invention, and the conventional PZT thin film.

[Drawing 4] Drawing showing the overPbO presentation ratio Y dependency of the piezoelectric constant d_{31} at the time of fixing to Zr presentation ratio $X = 0.45$ of the example of this invention, and the conventional PZT thin film.

[Drawing 5] The sectional view of the ferroelectric thin film in the example of this invention.

[Drawing 6] Drawing of the X diffraction pattern of the PZT thin film in the example of this invention.

[Drawing 7] Drawing showing the Zr presentation ratio X dependency of the specific inductive capacity epsilon of the example of this invention, and the conventional PZT thin film.

[Drawing 8] Drawing showing the overPbO presentation ratio Y dependency of the specific inductive capacity epsilon at the time of fixing to Zr presentation ratio $X = 0.60$ of the example of this invention, and the conventional PZT thin film.

[Description of Notations]

101 ... Single crystal Si substrate

102 ... SiO₂ film

103 ... Ti layer

104 ... Pt lower electrode

105 ... PZT film

106 ... Ti layer

107 ... Au electrode

108 ... Opening

201 ... Single crystal MgO substrate

202 ... Pt lower electrode

203 ... PZT film

204 ... Ti layer

205 ... Au electrode

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

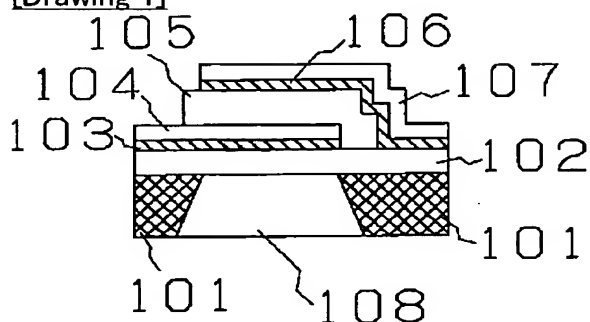
1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.*** shows the word which can not be translated.

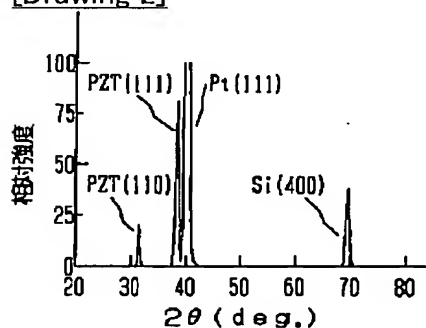
3.In the drawings, any words are not translated.

DRAWINGS

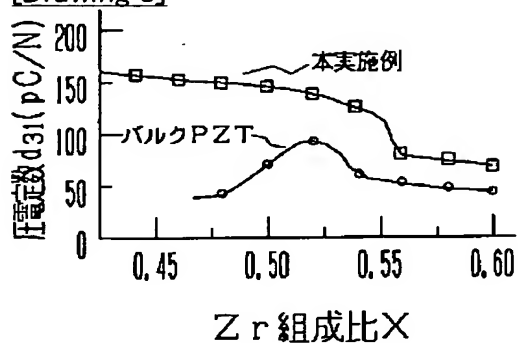
[Drawing 1]



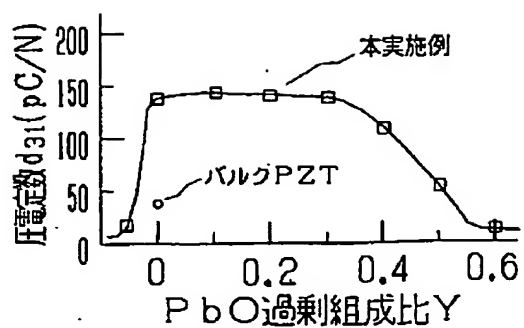
[Drawing 2]



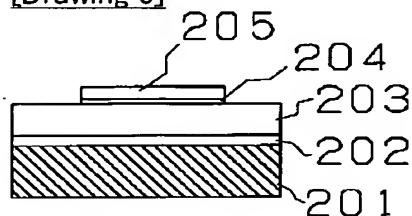
[Drawing 3]



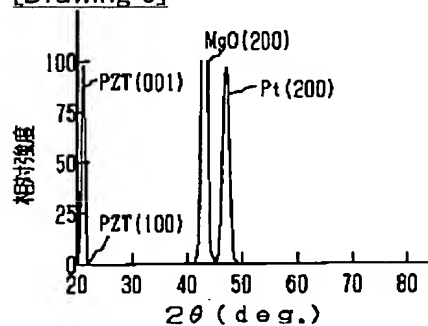
[Drawing 4]



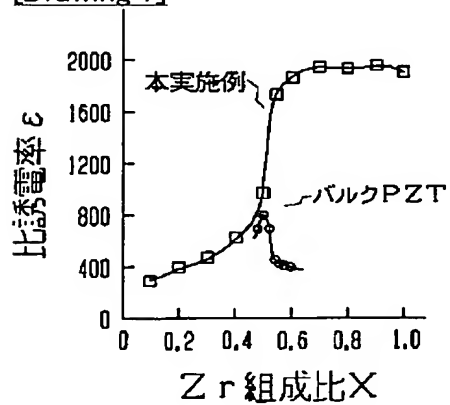
[Drawing 5]



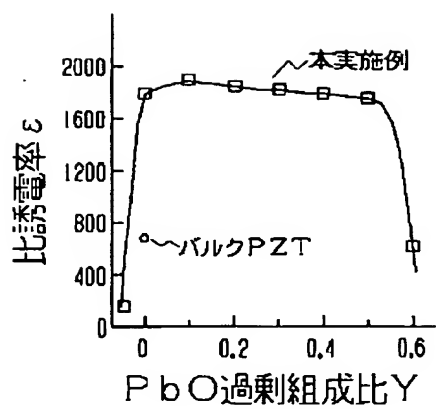
[Drawing 6]



[Drawing 7]



[Drawing 8]



[Translation done.]

*** NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. *** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law
[Category partition] The 2nd partition of the 7th category
[Publication date] June 29, Heisei 13 (2001. 6.29)

[Publication No.] JP,6-350154,A
[Date of Publication] December 22, Heisei 6 (1994. 12.22)
[Annual volume number] Open patent official report 6-3502
[Application number] Japanese Patent Application No. 5-137892
[The 7th edition of International Patent Classification]

H01L 41/08
C01G 25/00
H01L 37/02
// G01J 1/02

[FI]

H01L 41/08 Z
C01G 25/00
H01L 37/02
G01J 1/02 Y

[Procedure amendment]
[Filing Date] June 6, Heisei 12 (2000. 6.6)
[Procedure amendment 1]
[Document to be Amended] Description
[Item(s) to be Amended] Claim
[Method of Amendment] Modification
[Proposed Amendment]
[Claim(s)]

[Claim 1] It is the piezo electric crystal thin film which possesses a titanic-acid lead zirconate thin film on the substrate with which the metal membrane was formed.

The piezo electric crystal thin film whose crystal structure it is the range of $0 \leq X < 0.55$ and $0 \leq Y \leq 0.5$, and is a rhombohedral system when the chemical formula of said titanic-acid lead zirconate thin film is expressed with $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$.

[Claim 2] The piezo electric crystal thin film in which the diffraction reinforcement of {111} side bearing is carrying out orientation to 70% or more strongly in claim 1 among the diffraction reinforcement of said titanic-acid lead zirconate thin film of the direction of a principal plane of said substrate measured with the wide angle X-ray diffraction method.

[Claim 3] It is the piezo electric crystal thin film which possesses a titanic-acid lead zirconate thin film on the substrate with which the metal membrane was formed.

The piezo electric crystal thin film whose crystal structure it is the range of $0.55 \leq X < 1$ and $0 \leq Y \leq 0.5$, and is tetragonal system when the chemical formula of said titanic-acid lead zirconate

thin film is expressed with $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$.

[Claim 4] The piezo electric crystal thin film in which the diffraction reinforcement of {001} side bearing is carrying out orientation to 70% or more strongly in claim 3 among the diffraction reinforcement of said titanate-acid lead zirconate thin film of the direction of a principal plane of said substrate measured with the wide angle X-ray diffraction method.

[Claim 5] It is the piezo electric crystal thin film in which it sets they to be [any of claims 1-4], and said titanate-acid lead zirconate thin film contains the impurity not more than 15 mol %.

[Claim 6] It is the piezo electric crystal thin film said whose impurity is at least one sort of Nb, La, Ta, Nd, W, Mo, Mn, Ba, Sr, calcium, and Bi in claim 5.

[Claim 7] The piezo electric crystal thin film which sets they to be [any of claims 1-6], and is characterized by a metal membrane being in any of platinum, gold, a platinumiridium, platinum palladium, platinum nickel, and platinum titanium.

[Claim 8] The fluid injector characterized by providing which piezo electric crystal thin film of claims 1-7.

[Procedure amendment 2]

[Document to be Amended] Description

[Item(s) to be Amended] 0009

[Method of Amendment] Modification

[Proposed Amendment]

[0009] Then, this invention solves such a technical problem and a piezo-electric property, a ferroelectric property, and a pyroelectric property aim at offering a good piezo electric crystal thin film.

[Procedure amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] 0010

[Method of Amendment] Modification

[Proposed Amendment]

[0010]

[Means for Solving the Problem] Piezo electric crystal thin film of this invention It is the piezo electric crystal thin film which possesses a titanate-acid lead zirconate thin film on the substrate with which the metal membrane was formed. When the chemical formula of said titanate-acid lead zirconate thin film is expressed with $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$, It is characterized by being the range of $0 \leq X < 0.55$ and $0 \leq Y \leq 0.5$, and the crystal structure being a rhombohedral system, and sets above. Diffraction reinforcement of {111} side bearing is characterized by carrying out orientation to 70% or more strongly among the diffraction reinforcement of said titanate-acid lead zirconate thin film of the direction of a principal plane of said substrate measured with the wide angle X-ray diffraction method. Moreover, it is the piezo electric crystal thin film which possesses a titanate-acid lead zirconate thin film on the substrate with which the metal membrane was formed. It is characterized by being the range of $0.55 \leq X < 1$ and $0 \leq Y \leq 0.5$, and the crystal structure being tetragonal system, when the chemical formula of said titanate-acid lead zirconate thin film is expressed with $Pb_{1+Y}(ZrXTi_{1-X})O_{3+Y}$, and sets above. Diffraction reinforcement of {001} side bearing is characterized by carrying out orientation to 70% or more strongly among the diffraction reinforcement of said titanate-acid lead zirconate thin film of the direction of a principal plane of said substrate measured with the wide angle X-ray diffraction method. Moreover, in the above, said titanate-acid lead zirconate thin film carries out the description of containing the impurity not more than 15 mol %. Moreover, in the above, said impurity is characterized by being at least one sort of Nb, La, Ta, Nd, W, Mo, Mn, Ba, Sr, calcium, and Bi. Moreover, in the above, it is characterized by a metal membrane being in any of platinum, gold, a platinumiridium, platinum palladium, platinum nickel, and platinum titanium. The fluid injector of this invention is characterized by providing the above-mentioned piezo electric crystal thin film.

[Procedure amendment 4]

[Document to be Amended] Description

[Item(s) to be Amended] 0011

[Method of Amendment] Deletion

[Procedure amendment 5]

[Document to be Amended] Description

[Item(s) to be Amended] 0012

[Method of Amendment] Deletion

[Procedure amendment 6]

[Document to be Amended] Description

[Item(s) to be Amended] 0013

[Method of Amendment] Deletion

[Procedure amendment 7]

[Document to be Amended] Description

[Item(s) to be Amended] 0077

[Method of Amendment] Modification

[Proposed Amendment]

[0077]

[Effect of the Invention] According to the piezo electric crystal thin film of this invention the above passage, as compared with PZT of bulk, a piezo-electric property, strong dielectric characteristics, and a pyroelectric property can be raised by leaps and bounds. Moreover, since it is a thin film, it can manufacture easily with a spatter, a chemistry gaseous layer grown method, etc. Moreover, it is applicable to piezoelectric devices, such as a thin film piezoelectric transducer and a fluid injector, a semiconductor memory, a pyroelectric infrared detector, etc.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平6-350154

(43) 公開日 平成6年(1994)12月22日

(51) Int.Cl. ⁵	識別記号	庁内整理番号	F I	技術表示箇所
H 0 1 L 41/08				
C 0 1 G 25/00				
H 0 1 L 37/02				
// G 0 1 J 1/02	Y	7381-2G 9274-4M	H 0 1 L 41/ 08 審査請求 未請求 請求項の数4	Z O L (全 6 頁)

(21) 出願番号 特願平5-137892

(22) 出願日 平成5年(1993)6月8日

(71) 出願人 000002369

セイコーエプソン株式会社

東京都新宿区西新宿2丁目4番1号

(72) 発明者 島田 勝人

長野県諏訪市大和3丁目3番5号セイコー

エプソン株式会社内

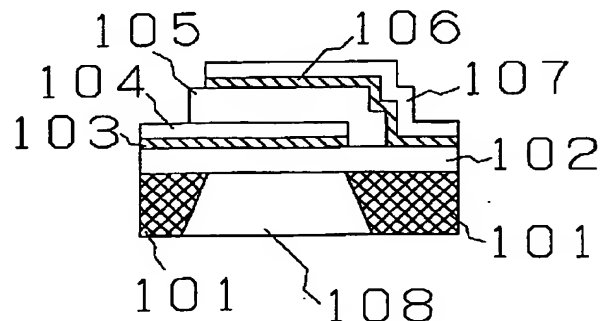
(74) 代理人 弁理士 鈴木 喜三郎 (外1名)

(54) 【発明の名称】 圧電体薄膜素子

(57) 【要約】

【目的】 圧電特性、強誘電体特性、焦電特性を向上することである。

【構成】 $\langle 111 \rangle$ 配向 P t 膜が形成された基板上に、化学式が $P b_{1-Y} (Z r_x T i_{1-x}) O_{3+Y}$ で、組成比が、 $0 \leq X < 0.55$ 、 $0 \leq Y \leq 0.5$ の範囲にあり、結晶構造が菱面体晶系のチタン酸ジルコン酸鉛膜であって、前記基板の主面垂直方向に対して、前記チタン酸ジルコン酸鉛膜の $\langle 111 \rangle$ 配向度が70%以上である圧電体薄膜素子。または、 $\langle 100 \rangle$ 配向 P t 膜が形成された基板の上に、化学式が $P b_{1-Y} (Z r_x T i_{1-x}) O_{3+Y}$ で、組成比が、 $0.55 \leq X < 1$ 、 $0 \leq Y \leq 0.5$ の範囲にあり、結晶構造が正方晶系のチタン酸ジルコン酸鉛膜であって、前記基板の主面垂直方向に対して、前記チタン酸ジルコン酸鉛膜の $\langle 001 \rangle$ 配向度が70%以上である圧電体薄膜素子。



【特許請求の範囲】

【請求項1】 金属膜が形成された基板上に、化学式が $Pb_{1-Y}(Zr_xTi_{1-x})O_{3-Y}$ で、組成比が、 $0 \leq X < 0.55$ 、 $0 \leq Y \leq 0.5$ の範囲にあり、結晶構造が菱面体晶系のチタン酸ジルコン酸鉛膜であって、前記基板の主面垂直方向に対して、前記チタン酸ジルコン酸鉛膜の $\langle 111 \rangle$ 配向度が70%以上であることを特徴とする圧電体薄膜素子。

【請求項2】 金属膜が、白金(Pt)、金(Au)または、PtまたはAuを主成分とする膜であって、前記基板の主面垂直方向に対して、 $\langle 111 \rangle$ 配向膜であることを特徴とする請求項1記載の圧電体薄膜素子。

【請求項3】 金属膜が形成された基板上に、化学式が $Pb_{1-Y}(Zr_xTi_{1-x})O_{3-Y}$ で、組成比が、 $0.55 \leq X < 1$ 、 $0 \leq Y \leq 0.5$ の範囲にあり、結晶構造が正方晶系のチタン酸ジルコン酸鉛膜であって、前記基板の主面垂直方向に対して、前記チタン酸ジルコン酸鉛膜の $\langle 001 \rangle$ 配向度が70%以上であることを特徴とする圧電体薄膜素子。

【請求項4】 金属膜が、白金(Pt)、金(Au)または、PtまたはAuを主成分とする膜であって、前記基板の主面垂直方向に対して、 $\langle 100 \rangle$ 配向膜であることを特徴とする請求項3記載の圧電体薄膜素子。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は薄膜圧電振動子、液体噴射装置等の圧電素子、半導体記憶装置、焦電型赤外線検出器等に用いられる強誘電体薄膜装置に関する。

【0002】

【従来の技術】本発明にかかわる従来技術は、例えば、特開昭62-252005が開示されている。

【0003】前記従来技術によると、化学式が $Pb_{1-Y}(Zr_xTi_{1-x})O_{3-Y}$ の場合において、組成比が、 $0 \leq X < 0.55$ 、 $Y=0$ の範囲に限定されており、バルクが多結晶体のチタン酸ジルコン酸鉛(PZT)に於いて、結晶構造が正方晶系の化学量論的組成に限定されていた。

【0004】更に、Zr組成比Xが0から0.55の範囲に限られており、PZTの結晶粒の中のドメインの自発分極の75%以上が一方を向いていた。

【0005】

【発明が解決しようとする課題】しかしながら、前記従来技術を用いた強誘電体薄膜素子には以下に示す問題点が存在する。

【0006】PZTのPb組成比が $Pb/(Zr+Ti)=1$ と化学量論的組成であるため、製造方法が困難である。

【0007】特に、Pbを含む化合物の場合、焼成、焼結、またはスパッタ法等の成膜時の高温処理時にPbOの形で、Pbが抜けやすく、化学量論的組成に制御する

ことは、非常に困難である。

【0008】更に、ほとんどの圧電素子、半導体記憶装置、焦電型赤外線検出器素子においては、成膜後に分極処理をする事が許されるため、Zr組成比Xが $0 \leq X < 0.55$ の範囲に限られる必要がない。

【0009】そこで、本発明はこのような課題を解決するもので、その目的とするところは、最適な結晶配向性及び組成を持ったPZT薄膜を用いて、圧電特性、強誘電体特性、焦電特性を向上することである。

【0010】

【課題を解決するための手段】上記問題点を解決するために、

(1) 本発明の圧電体薄膜素子は、金属膜が形成された基板上に、化学式が $Pb_{1-Y}(Zr_xTi_{1-x})O_{3-Y}$ で、組成比が、 $0 \leq X < 0.55$ 、 $0 \leq Y \leq 0.5$ の範囲にあり、結晶構造が菱面体晶系のチタン酸ジルコン酸鉛膜であって、前記基板の主面垂直方向に対して、前記チタン酸ジルコン酸鉛膜の $\langle 111 \rangle$ 配向度が70%以上であることを特徴とする。

【0011】(2)更に、上記金属膜が、白金(Pt)、金(Au)または、PtまたはAuを主成分とする膜であって、前記基板の主面垂直方向に対して、 $\langle 111 \rangle$ 配向膜であることが望ましい。

【0012】あるいは、(3) 本発明の圧電体薄膜素子は、金属膜が形成された基板上に、化学式が $Pb_{1-Y}(Zr_xTi_{1-x})O_{3-Y}$ で、組成比が、 $0.55 \leq X < 1$ 、 $0 \leq Y \leq 0.5$ の範囲にあり、結晶構造が正方晶系のチタン酸ジルコン酸鉛膜であって、前記基板の主面垂直方向に対して、前記チタン酸ジルコン酸鉛膜の $\langle 001 \rangle$ 配向度が70%以上であることを特徴とする。

【0013】(4)更に、上記金属膜が、白金(Pt)、金(Au)または、PtまたはAuを主成分とする膜であって、前記基板の主面垂直方向に対して、 $\langle 100 \rangle$ 配向膜であることが望ましい。

【0014】

【実施例】(実施例1)以下、本発明の実施例を図面に基づいて説明する。

【0015】図1は、本発明に従って作成した強誘電体薄膜素子の第1の実施例である薄膜圧電振動子の断面図である。

【0016】(100)面単結晶Si基板101に、熱酸化を行い、 $1\mu m$ のSiO₂膜102を形成する。

【0017】前記SiO₂膜102上に、膜厚50ÅのTi層103と膜厚3000ÅのPt下部電極104を直流スパッタリングにより形成した。

【0018】スパッタは、Ar雰囲気、200℃の基板温度で行った。

【0019】Pt下部電極104は、Si基板101の主面垂直方向に対して、 $\langle 111 \rangle$ 配向している。

【0020】次にPZT膜105を $2\mu m$ 、高周波スパ

ッタ法により形成した。

【0021】スパッタは、ArとO₂雰囲気、200℃の基板温度で行った。

【0022】スパッタリングターゲットには、Pb_{1-y}(Zr_xTi_{1-x})O_{3+y}を用いた。

【0023】ここで、Y=0.3、X=0.5である。

【0024】次いで、ペロブスカイト結晶構造のPZTを得るために、O₂雰囲気中、600℃で、3時間熱処理を行った。

【0025】次いで、PZT膜上に膜厚100ÅのTi層106、及び膜厚2000ÅのAu電極107を順次蒸着し、最後に、PZT膜105の下部に於ける単結晶Si基板101にSiO₂膜102に至るまで開口部108を設け、強誘電体薄膜素子を作成した。

【0026】図2に、代表的なPZT薄膜のX線回折パターンを示す。

【0027】Si基板の反射ピークとPt下部電極の反射ピーク以外は、ペロブスカイト構造のPZTの反射ピークである。

【0028】図2に示された本実施例の過剰鉛組成比Yは、0.05、Zr組成比Xは、0.50であり、〈111〉配向度は、80%であった。

【0029】ここで、〈111〉配向度P(111)は、 $P(111) = I(111) / \sum I(hkl)$ で表す。

【0030】 $\sum I(hkl)$ は、X線回折(XRD)法の高角反射法で、波長にCuK α 線を用いたときの2 θ が20度〜80度のPZTの全回折強度の和を表す。

【0031】具体的には、(100)、(110)、(111)、(210)、(211)、(221)、(310)結晶面反射強度の総和である。

【0032】I(111)は、同じくPZTの(111)結晶面反射強度を表す。

【0033】図3は〈111〉方向に70から100%配向した膜厚2 μ mのPZT薄膜の圧電定数d₃₁のZr組成比X依存性を示す。

【0034】PbO過剰組成比Yは、0.05である。

【0035】図3中に比較のため、バルクPZTの圧電定数も示した。

【0036】図3に示すように、全組成範囲に於いて、バルクのPZTの圧電定数より、70から100%〈111〉配向したPZT薄膜の圧電定数は、大きな値を示した。

【0037】特に、Zr組成比Xが、0から0.55の範囲に於いて、バルクPZTに比較して、飛躍的に大きい値を示した。

【0038】これは、バルクPZTの結晶構造が、この組成範囲で、正方晶系で有るのに対して、配向薄膜の場合は、菱面体晶系となることによると考えられる。

【0039】すなわち、バルクPZTの菱面体晶系組成

の範囲、すなわちZr組成比Xが0.55から1の範囲では、組成比Xが小さいほど圧電定数が大きくなるが、薄膜の場合には、更にXが0から0.55の範囲まで及んであるためだろう。

【0040】図4には、Zr組成比X=0.45に固定した場合の圧電定数d₃₁のPbO過剰組成比Y依存性を示す。

【0041】PZT薄膜の膜厚は、同じく2 μ m、〈111〉配向度は、70から100%である。

【0042】図4に示すように、圧電定数d₃₁は、PbOの過剰分Yに大きく依存しており、Yが0より小さいと急激に低下し、Y=0.5より大では、バルクPZT並みまで低下する。

【0043】Yが0.5より大きくなると圧電定数d₃₁が小さくなる理由としては、粒界へのPbOの析出であることがわかった。

【0044】従って、Yの範囲は、0以上0.5以下であることが望ましい。

【0045】以上実施例1に於いて、下部電極として、〈111〉配向Ptを用いて説明したが、PZT薄膜の〈111〉配向度が、70%以上となれば良く、Au、Pt-Ir、Pt-Pd、Pt-Ni、Pt-Ti等他の金属膜でも良い。

【0046】更に、実施例1では、薄膜圧電振動子を例に取り説明したが、液体噴射装置、半導体記憶装置、焦電型赤外線検出器等にもそのまま応用できることは自明である。

【0047】(実施例2)以下、本発明の実施例を図面に基づいて説明する。

【0048】図5は、本発明に従って作成した強誘電体薄膜素子の第2の実施例の断面図である。

【0049】(100)面単結晶MgO基板201に、高周波スパッタ法により、MgO基板201の主面方向に対して〈100〉配向のPt下部電極202を形成する。

【0050】スパッタは、Ar/O₂=8/2の雰囲気中、200℃の基板温度で行った。

【0051】次にPZT膜203を2 μ m、高周波スパッタ法により形成した。

【0052】スパッタは、ArとO₂雰囲気、700℃の基板温度で行った。

【0053】スパッタリングターゲットには、Pb_{1-y}(Zr_xTi_{1-x})O_{3+y}を用いた。

【0054】ここで、Y=0.5、X=0.6である。

【0055】高温スパッタにより、アズースパッタで、ペロブスカイト結晶構造のPZTを得ることができた。

【0056】次いで、PZT膜上に膜厚100ÅのTi層204、及び膜厚2000ÅのAu電極205を順次蒸着し、特性を評価した。

【0057】図6に、代表的なPZT薄膜のX線回折パ

ターンを示す。

【0058】MgO単結晶基板の反射ピークとPt電極の反射ピーク以外は、ペロブスカイト構造のPZTの反射ピークである。

【0059】図6に示された本実施例の過剰鉛組成比Yは、0.10、Zr組成比Xは、0.60であり、 $\langle 001 \rangle$ 配向度は、98%であった。

【0060】ここで、 $\langle 001 \rangle$ 配向度P(001)は、 $P(001) = I(001) / \sum I(hkl)$ で表す。

【0061】図7は $\langle 001 \rangle$ 方向に70から100%配向した膜厚2 μ mのPZT薄膜の比誘電率 ϵ のZr組成比X依存性を示す。

【0062】ここで示す比誘電率 ϵ は、膜厚方向に分極処理した後の膜厚方向の比誘電率である。

【0063】PbO過剰組成比Yは、0.10である。

【0064】図7中に比較のため、バルクPZTの比誘電率 ϵ も示した。

【0065】図7に示すように、全組成範囲に於いて、バルクのPZTの比誘電率 ϵ より、70から100% $\langle 001 \rangle$ 配向したPZT薄膜の比誘電率 ϵ は、大きな値を示した。

【0066】特に、Zr組成比Xが、0.55から1の範囲に於いて、バルクPZTに比較して、飛躍的に大きい値を示した。

【0067】これは、バルクPZTの結晶構造が、この組成範囲で、菱面体晶系で有るのに対して、配向薄膜の場合は、正方晶系となることによると考えられる。

【0068】すなわち、バルクPZTの正方晶系組成の範囲、すなわちZr組成比Xが0から0.55の範囲では、組成比Xが大きいくほど比誘電率が大きくなるが、薄膜の場合には、更にXが0.55から1の範囲まで及んであるためだろう。

【0069】図8に、Zr組成比X=0.60に固定した場合の比誘電率 ϵ のPbO過剰組成比Y依存性を示す。

【0070】PZT薄膜の膜厚は、同じく2 μ m、 $\langle 001 \rangle$ 配向度は、95から100%である。

【0071】比較のためバルクPZTの比誘電率も示す。

【0072】図8に示すように、比誘電率 ϵ は、PbOの過剰分Yに大きく依存しており、Yが0より小さいと急激に低下し、Y=0.5より大では、バルクPZT並みまたは、それ以下まで低下する。

【0073】従って、Yの範囲は、0以上0.5以下であることが望ましい。

【0074】以上実施例2に於いて、下部電極として、 $\langle 100 \rangle$ 配向Ptを用いて説明したが、PZT薄膜の $\langle 001 \rangle$ 配向度が、70%以上となれば良く、Au、Pt-Ir、Pt-Pd、Pt-Ni、Pt-Ti等他

の金属膜でも良い。

【0075】以上上記実施例1、2に於いて、圧電膜として、純粋な組成のPZT薄膜を用いて説明したが、勿論若干の不純物が混入されていてもさしつかえない。

【0076】不純物としては、一般的に圧電性を向上するものとして、Nb、La、Ta、Nd、W、Mo、Mn、Ba、Sr、Ca、Bi等があり、15モル%以下を加えることは可能である。

【0077】

10 【発明の効果】以上述べてきたように本発明の圧電体薄膜素子は、以下のような効果を有する。最適な結晶配向性及び組成を持ったPZT薄膜を用いることにより、バルクのPZTに比較して飛躍的に、圧電特性、強誘電体特性、焦電特性を向上することができ、更に薄膜であるため、スパッタ法や化学気相成長法等で製造できるので、作成が容易であり、薄膜圧電振動子、液体噴射装置等の圧電素子、半導体記憶装置、焦電型赤外線検出器等に応用することができる。

【図面の簡単な説明】

20 【図1】本発明の実施例における薄膜圧電振動子の断面図。

【図2】本発明の実施例における、PZT薄膜のX線回折パターン図。

【図3】本発明の実施例及び従来のPZT薄膜の圧電定数 d_{31} のZr組成比X依存性を示す図。

【図4】本発明の実施例及び従来のPZT薄膜の、Zr組成比X=0.45に固定した場合の圧電定数 d_{31} のPbO過剰組成比Y依存性を示す図。

30 【図5】本発明の実施例における強誘電体薄膜素子の断面図。

【図6】本発明の実施例における、PZT薄膜のX線回折パターン図。

【図7】本発明の実施例及び従来のPZT薄膜の比誘電率 ϵ のZr組成比X依存性を示す図。

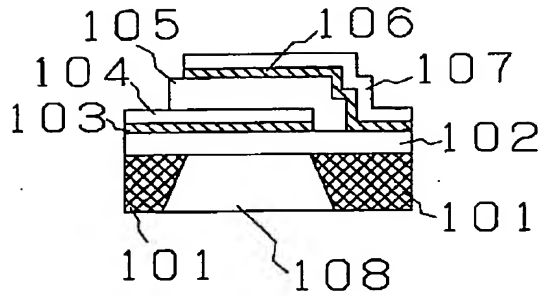
【図8】本発明の実施例及び従来のPZT薄膜の、Zr組成比X=0.60に固定した場合の比誘電率 ϵ のPbO過剰組成比Y依存性を示す図。

【符号の説明】

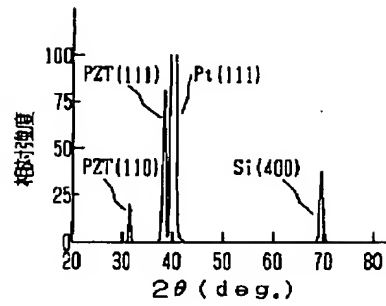
101・・・単結晶Si基板
102・・・SiO₂膜
103・・・Ti層
104・・・Pt下部電極
105・・・PZT膜
106・・・Ti層
107・・・Au電極
108・・・開口部
201・・・単結晶MgO基板
202・・・Pt下部電極
203・・・PZT膜
50 204・・・Ti層

205...Au電極

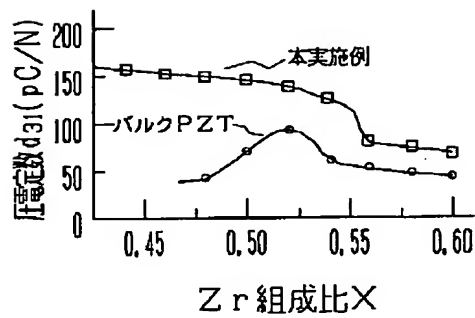
【図1】



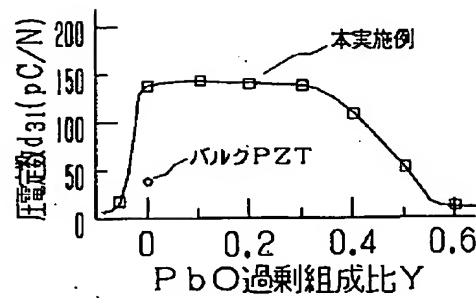
【図2】



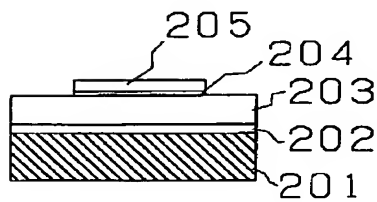
【図3】



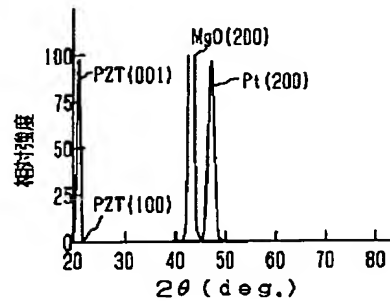
【図4】



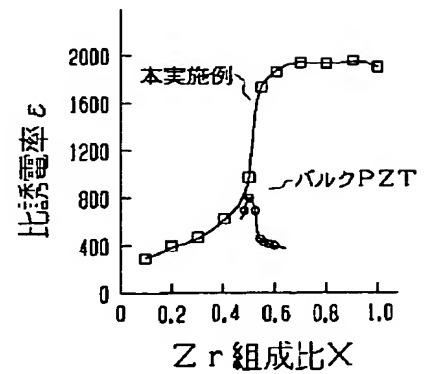
【図5】



【図6】



【図7】



【図8】

